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(54) RESINOUS MOULDING COMPOSITIONS CONTAINING REINFORCING MATERIAL

(71) We, THE GLASS MANUFACTURERS FEDERATION, a Trade Association incorporated and limited by guarantee under Section 19 of the Companies Act 1948, of 19 Portland Place, London W1N 4BH and UNIVERSITY COLLEGE CARDIFF, a British Registered Charity and Body Corporate, of P.O. Box: 78, Cardiff CF1 1XL, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to moulding compositions, and to moulded articles made therefrom.

Moulding compositions including resinous binders and reinforcing material are very well known. It is known that the resinous binders may be of a thermoplastic or thermosetting resin, and that many types of addenda are usable. Thus, many types of filler are known, ranging from naturally occurring particulate materials such as talc and chalk to man-made fibrous materials such as nylon fibres. Glass-reinforced plastics (GRP) are widely used nowadays for very many purposes, including for example the manufacture of motor-car bodies and boat hulls. These GRP's normally consist of a thermosetting resinous binder, e.g. an unsaturated polyester and a copolymerisable monomer, reinforced with glass fibres. Other fillers, e.g. calcium carbonate, may also be present.

It is an object of the present invention to provide a novel moulding composition. It is a further object of the invention to provide a use for waste glass, in particular used glass containers such as jars and bottles.

According to the present invention a moulding composition comprises a curable resinous material and glass chippings.

By "glass chippings" we mean pieces of glass at least the majority, and preferably all, of which have particle sizes within the range 0.5—10 mm. We do not intend glass fibres to be comprehended within the meaning of "glass chippings", nor do we intend powdered glass in very finely divided form to be so comprehended. The glass chippings are obtained by crushing waste glass, for example used and discarded glass bottles. Glass bottles and other glass containers are used for packaging a variety of products, which use often requires them to be made of coloured glass, e.g. amber glass for beer bottles and green glass for wine bottles. By the use of different coloured glass chippings, and mixtures of them, we can produce moulding compositions of varying colours and mixtures of colours, which colours and mixtures of colours may be reproduced in the ultimate moulded product made therefrom. Particularly suitable glass chippings are those wherein at least the majority have particle sizes in the range 1.2—7.0 mm., and especially useful are those having particle sizes in the range 1.4—6.8 mm. This range represents mesh sizes of 3 to 6 (6 mm.—2.8 mm) and 6 to 12 (2.8 mm.—1.4 mm).

The curable resinous material may be a thermoplastic resin, but preferably it is a thermosetting resin. Preferably also it is a "cold-cure" thermosetting resin. Examples of suitable resins include phenolics, aminoplasts (e.g. ureaformaldehyde resins), epoxies and, preferably, polyesters. Mixtures of resins, for example rigid and flexible resins, may also be used. It will be appreciated that the moulding compositions of the present invention may include not only the resinous material and the glass chippings but also any curing catalysts, inert or reactive diluents, stabilisers, antioxidants and other fillers and materials commonly used in such resins, as desired. It is sometimes desirable to add to the resinous material a pigment or pigmented glass powder to impart background

colour to the ultimate moulded product. Such pigments as Monastral Blue and Monolite Red 4RS are useful in this respect. "Monastral" and "Monolite" are trade marks.

Particularly suitable polyester resins for use in the moulding compositions of the present invention are those sold by B.P. International Limited under the trade designations A2622 (a rigid resin) and A2593 (a flexible resin). These are both orthophthalic resins crosslinked with styrene. Suitable resin mixes comprise up to 20% by weight of flexible resin, based on the total weight of resin. The moulding composition will normally also contain a cobalt promoter and a curing catalyst, e.g. methyl ethyl ketone peroxide which will cause the resin to set at room temperature in 30—45 mins. Post-curing can be carried out for periods of up to 2 hours at temperatures of the order of 120°C.

The moulding composition may comprise between 50 and 90%, by weight, of glass chippings, suitably 70—80% on the same basis. The colour of the glass chippings may be dependent upon what waste glass is available, and if it be glass from discarded glass containers the chippings will normally be of white glass (i.e. transparent), amber glass (brown) or dark green glass. Other possible colours are blue and opal. Alternatively, use may be made of the technique described in our copending Application No. 35499/77 wherein we have described a method for fixing surface colours to glass chippings according to which, for example, red, white or blue glass may be prepared from white glass. The glass colour will be selected in dependence upon the moulded article which it is desired to manufacture.

The compositions of the invention are especially useful for the manufacture of decorative articles such as wall tiles, floor tiles, cast floors, wall panels, table tops, decorative screens, working surfaces, roof lights and "works of art", e.g. miniatures.

We have found that because of the high bonding property of glass and its ability to absorb the heat generated by the cure of the resin (when this is thermosetting) it is possible to cast items of larger bulk than has hitherto been possible with conventional reinforced moulding materials, without distortion or cracking of the final product.

The moulding compositions are made by simple admixture of the ingredients in the desired proportions. If the catalyst is a cold-setting catalyst, then either the catalyst will be omitted from the composition and sold, and supplied, separately, or the composition will be compounded shortly before use. It is preferred that before they are incorporated into the moulding composition the glass chippings are treated with a material which will enhance the glass-resin bond and hence increase the strength of the moulded product. In one embodiment the glass is treated with a silane coupling agent, such as that sold under the trade designation Z6032 by Dow Corning International. This material is a 40% by weight solution of a silane in methanol; suitably the glass is treated with the coupling agent at the rate of 0.5% by weight on the weight of glass, in water adjusted to and maintained acid, e.g. at a pH value of 4, with acetic acid. The volume of treating solution is preferably such as to give a coating on the treated glass of 2% by weight silane based on the weight of the glass. Treatment will normally be for 10—20 mins. e.g. about 15 mins. after which the glass is drained of treating solution and dried, for example for 1 hour at 105°C.

In one method of manufacturing wall tiles, a weighed amount of glass chippings is placed and suitable dispersed in a mould (which is suitably made from pieces of sheet glass but which can also be made from material having an irregular surface, to provide an embossed surface on the final product) and a quantity of resin, e.g. polyester resin, mixed with promoter and catalyst is poured evenly over the glass in the mould. When the resin has cured the finished product is removed from the mould. In an alternative procedure, resin is sprayed into the mould, or on a surface to be decorated, whereafter the glass chippings are sprayed or "thrown" onto the resin which thereafter is allowed to cure. In yet another procedure, a mixture of resin and glass chippings is charged into a mould of suitable shape and size, and allowed to cure. A mould consisting of two pieces of glass held a fixed distance apart by a sealing gasket will enable the production of a moulding having two smooth surfaces.

Tiles have been made from moulding compositions of the following formulations, by weight:—

Mesh Size.	*%Glass.*	*%Resin.*
3—6 (6.8—2.8 mm)	79	21
6—12 (2.8—1.4 mm)	73	27
6—150 (1.4 mm and smaller)	75	25

To one or both surfaces of the final product, e.g. a tile or wall panel, may be attached a slab, of any desired thickness, of foamed material. Such material may be preformed, or alternatively foamed *in situ*. Suitable foamed materials include polyurethane, polystyrene and phenolic foams, and their use imparts to the final product a degree of thermal and/or sound insulation. In one method, two panels are made from the moulding composition of the invention; these are then held vertically, e.g. in a jig, horizontally spaced apart and with an edge seal; a foamable mixture is then poured into the open-topped container so formed and is allowed, or caused, to foam *in situ*. A suitable foamable mix is that sold by Strand Glass Fibres Limited.

The drawing accompanying the Provisional Specification is a diagrammatic illustration of a wall tile made according to the invention containing glass chippings 1 rigidly bound together in a resinous binder 2.

The following Examples are given for the purpose of illustrating the invention.

Example 1

A mould was made from a piece of plain glass 25 cms×25 cms×3 mms, the edges of one face of which were built up with strips of glass of a similar thickness to give a shallow trough having internal dimensions of 18 cms×18 cms×3 mms. The interior of this trough was treated with a solution of paraffin wax in hexane (or with a proprietary brand of slip wax).

220 g of silane-treated 3—6 mesh glass chippings were spread evenly over the mould and 60 g of resin mix containing catalyst and promotor poured on top. The composition was allowed to cure in air for 2 hours, after which the partly cured tile so formed was removed from the mould and laid on a flat surface in an oven at 105°C for post-curing. This was effected for 2 hours.

Glass/Resin ratio for this tile was 3.67 : 1 (78.5% w/w glass or 61.68% v/v glass.

Example 2

A similar tile to that of Example 1 was made exactly as described therein except that 0.01 g of Monastral green pigment was mixed in with the resin before pouring. The tile had a delicate overall green colour.

Example 3

A mould was prepared of two waxed plates of glass of dimensions 20 cms× 20 cms×3 mms. A rubber gasket in the shape of a square "U" was clamped between the two plates to give an open top container of approximate internal dimensions 18 cms× 18 cms×8.5 mms.

Into this mould, held vertically, was poured 160 g of resin mix containing both catalyst and promoter. Any air bubbles were allowed a few minutes to rise to the surface and 405 g of silane-treated 3—6 mesh glass chippings were slowly poured into the resin.

After 2 hours the clamps were removed and the partly cured tile removed. Post curing was effected for 2 hours at 105°C.

This tile contained 71.68% w/w glass (52.65 : v/v).

The surface texture of the tile could be changed by increasing its resin content.

WHAT WE CLAIM IS:—

1. A moulding composition comprising a curable resinous material and glass chippings (as hereinbefore defined).

2. A composition as claimed in claim 1 wherein at least the majority of the glass chippings have particle sizes in the range 1.2 to 7.0 mm.

3. A composition as claimed in claim 1 or 2 wherein the glass chippings are formed by crushing waste glass containers.

4. A composition as claimed in any of claims 1 to 3 wherein the resinous material is a thermosetting resin.

5. A composition as claimed in claim 4 wherein the resinous material is an unsaturated polyester resin.

6. A composition as claimed in any of claims 1 to 5 containing also one or more of the following: a catalyst, a diluent, a stabiliser, an antioxidant, a pigment.

7. A composition as claimed in any of claims 1 to 6 wherein the glass chippings are present in an amount of 50 to 90%, by weight, based on the weight of the composition.

8. A composition as claimed in claim 7 wherein the glass chippings are present in an amount of 70 to 80%, on the same basis.

9. A composition as claimed in any of claims 1 to 8 in which the glass chippings are treated with a silane coupling agent.

10. A composition as claimed in claim 9 wherein the glass chippings contain up to 2% by weight silane as a surface coating.

11. A composition as claimed in claim 1, substantially as hereinbefore described.

12. A method of forming a shaped product which comprises forming into shape a composition as claimed in any preceding claim and causing or allowing the resinous material to cure.

13. A method as claimed in claim 12 wherein the resinous material is caused partially to cure in air and is then post-cured in an oven.

14. A method as claimed in claim 12, substantially as hereinbefore described in any of the Examples.

15. A shaped product formed by the method of any of claims 12 to 14.

16. A shaped product as claimed in claim 15 to which is adhered a thickness of foamed material.

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1588132 PROVISIONAL SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*